

Composition Control of Low-Volatility Solids Through Chemical Vapor Transport Reactions. I. Theory of Selective Chemical Vapor Transport

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A new method is proposed for controlling the composition (nonstoichiometry) of low-volatility inorganic compounds. It is based on the introduction/elimination of one of the components into/ from the low-volatility compound using reversible selective chemical vapor transport. The conditions for composition control through selective chemical vapor transport are deduced from the principles of nonequilibrium thermodynamics, in which the direction of the mass-transfer of a component is unambiguously defined by the temperature and composition of the source (T_1, x_1) and of the sample (T_2, x_2) . This approach can be employed to control the sample composition in a closed vapor-transport system, in which composition x_2 of the sample is defined by the fixed values of x_1 , T_1 , and T_2 , provided the steady-state (no mass-transfer) condition is achieved. The effect of steady-state conditions on sample composition is visualized using T_1 - x_2 diagram for the following system: sample (Ga-S phases)-vapor-charge (pure Ga).

Keywords binary system, experimental kinetics, experimental techniques, experimental thermodynamics, modeling, nonequilibrium processes

1. Introduction

$$\Delta n_q = m_p A^0_p - m_p C_q^0 - \frac{1}{4} q A_n C_m^0$$

Eq. 1b

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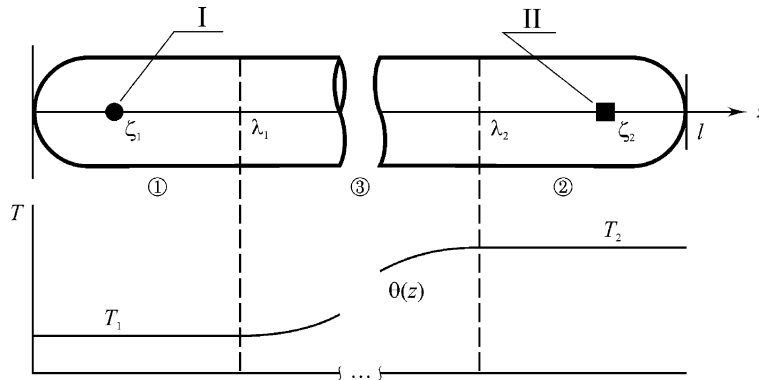


Fig. 1 Experiment for controlling composition of the sample by using selective chemical vapor transport (with the corresponding temperature profile). I indicates the charge, which serves as source or getter of the component to be transported; II indicates the sample.

1. Interaction of transporting component with only one of the components in the A_xB_y compound (e.g., component A) should: (a) supply comparable amounts of the forms A_pB_q and A_nC_m to the vapor phase and (b) quickly attain the equilibrium state.
2. No binary or ternary compounds of component with component B (which will not be transported) should exist in the ternary A-B-C system under experimental conditions (so-called indifference condition for component in respect to the component B).
3. Component C must be practically insoluble in A_xB_y compound.
4. A_xB_y compound must be nonvolatile at the experimental conditions.

$$2Ga^{00} + Ga^{0}_{3} \rightleftharpoons 3Ga^{0}$$

Eq 2

$$\mu_i \rightleftharpoons \mu_i + RT \ln p_i$$

Eq 3

$$RT \ln \kappa_p \rightleftharpoons 2\mu_{Ga}^{00} + F^{00}T$$

Eq 4

$$\kappa_p \rightleftharpoons p_{Ga}^3 = p_{Ga}^0$$

Eq 5

$$F^{00}T \rightleftharpoons \frac{1}{4}\mu_{Ga}^0 + 3\mu_{Ga}$$

Eq 6

2. Control of the Composition for Low-Volatility Gallium Selenides

$$\alpha_{P_1} \rightleftharpoons \alpha_{P_2}$$

Eq 7

$$0 \leq \zeta_1 < \lambda_1; \quad \lambda_2 < \zeta_1 \leq 1 \quad (1)$$

Eq 9

$$\dot{S}_1 \leq \frac{1}{T} A v \quad (10)$$

Eq 10

$$s_1 \leq \frac{1}{T} A v \delta \zeta_1 \quad \text{and} \quad s_2 \leq \frac{1}{T} A v \delta \zeta_2 \quad (11)$$

Eq 11

3. Stationary State in a Transport Nonisothermal System

$$s \leq \frac{1}{V} \lim_{V \rightarrow 0} \frac{S \delta V}{P \delta V}$$

$$s_3 \leq J_U r \left(\frac{1}{T} \right) \sum_k J_k r \left(\frac{\mu_k}{T} \right) \quad (12)$$

Eq 12

$$s_3 \leq \delta J_U - \sum_k J_k \mu_k r \left(\frac{1}{T} \right) - \frac{1}{T} \sum_k J_k r \mu_k \quad (13)$$

Eq 13

$$T \leq \begin{cases} T_1; 0 \leq \lambda_1 \\ 0 \leq \lambda_1 \leq \lambda_2; 0 \leq \lambda_1 \leq T_1; 0 \leq \lambda_2 \leq T_2 \\ T_2; \lambda_2 \leq 1 \end{cases} \quad (14)$$

Eq 14

$$r \mu_k \leq \frac{\partial \mu_k}{\partial T} r \leq \partial r \mu_k \quad (15)$$

Eq 15

$$J_Q \leq J_U - \sum_k J_k H_k \quad (16)$$

Eq 16

$$\dot{s}_3 \approx J_{QR} \left(\frac{1}{T} \right) - \frac{1}{T} \sum_k J_k \dot{\sigma} r_{\mu_k} p_T \quad \text{Eq 16}$$

$$C_{Gal}(r_{\mu_{Gal}})_T \neq C_{Gal}(r_{\mu_{Gal}})_T \approx 0 \quad \text{Eq 17}$$

$$J_{Gal} V_{Gal} \neq J_{Gal} V_{Gal} \approx 0 \quad \text{Eq 18}$$

$$\dot{s}_3 \approx J_{QR} \left(\frac{1}{T} \right) - \frac{1}{T} \frac{J_{Gal}}{\partial t} \frac{\dot{\sigma} r_{\mu_{Gal}}}{x_{Gal} p} p_T \quad \text{Eq 19}$$

$$\dot{s} \approx J_{QR} \left(\frac{1}{T} \right) - \frac{1}{T} \frac{J_{Gal}}{\partial t} \frac{\dot{\sigma} r_{\mu_{Gal}}}{x_{Gal} p} p_T \quad \text{Eq 20}$$

$$\neq \frac{1}{T} A v \sum_{\gamma} \delta \tilde{\alpha}_{\gamma} z \neq \quad \gamma = 1; 2$$

$$v_1 dA_1 \neq v_2 dA_2 = 0 \quad \text{Eq 24}$$

$$A_1 \approx \text{const} \quad A_2 \approx \text{const} \quad \text{or} \quad v_1 \approx 0; \quad v_2 \approx 0 \quad \text{Eq 25}$$

$$A_1 \approx 0; \quad A_2 \approx 0; \quad v_1 \approx 0; \quad v_2 \approx 0 \quad \text{Eq 26}$$

$$J_k \approx L_k X_k \quad \text{Eq 27}$$

$$\dot{S} \approx \int_V \dot{s} dV \quad \text{Eq 21}$$

$$\dot{S}_3 \approx \int_V \left(J_{QR} \left(\frac{1}{T} \right) - \frac{1}{T} \frac{J_{Gal}}{\partial t} \frac{\dot{\sigma} r_{\mu_{Gal}}}{x_{Gal} p} p_T \right) dV \quad \text{Eq 28}$$

$$\dot{S} \approx \int_0^l \left(J_{QR} \left(\frac{1}{T} \right) - \frac{1}{T} \frac{J_{Gal}}{\partial t} \frac{\dot{\sigma} r_{\mu_{Gal}}}{x_{Gal} p} p_T \right) dz = \sigma \neq \sum_{\gamma} \frac{1}{T_{\gamma}} A_{\gamma} v_{\gamma} \quad \text{Eq 22}$$

$$\dot{\sigma} r_{\mu_{Gal}} p_T \approx 0 \quad \text{Eq 29}$$

$$\dot{\sigma} r_{\mu_{Gal}} p_T \approx 0 \quad \text{Eq 30}$$

$$r_{p_{Gal}} \approx 0; \quad r_{p_{Gal}} \approx 0 \quad \text{Eq 31}$$

$$p_{Gal} \dot{\sigma} T_1 \neq p_{Gal} \dot{\sigma} T_2 \neq p_{Gal} \dot{\sigma} T_1 \neq p_{Gal} \dot{\sigma} T_2 \neq \quad \text{Eq 32}$$

$$\dot{S}' \approx \sum_{\gamma} \frac{1}{T_{\gamma}} A_{\gamma} v_{\gamma} \quad \text{Eq 23}$$

Table 1 The temperature dependence of α_p values for different equilibrium states in the Ga-S-I system and the boundary lines that limit areas of existence of different condensed phases at T_1 projection of T_2 - T_1 - x_2 diagram. In column 2, prime (') and double prime (") indicate vapor and condensed phases, respectively

1	2	3	4	5
Equilibrium phases (V = vapor GaI + GaI)	Equilibrium in a chemical subscription	Temperature (T), K	Temperature dependence of α_p [16,17]	Temperature dependence $T_2 = f(T_1)$. Calculated using Eq 7 and data of the column 4
GaI - V	$2GaI \rightleftharpoons Ga_2I \rightleftharpoons 3GaI$	727-1134	$\log \alpha_p = \frac{10329}{T} - 11.71$	$T_1 = T_2$
L ^{Ga} -GaS-V	$GaI \rightleftharpoons Ga_2I \rightleftharpoons 3GaI$	804-1065	$\log \alpha_p = \frac{11172}{T} - 12.45$	$T_1 = \frac{10329T_2}{11172 - 0.74T_2}$
GaS-Ga ₂ S ₃ -V	$6GaI \rightleftharpoons Ga_2I \rightleftharpoons 3GaI \rightleftharpoons 2Ga_2S_3$	873-1130	$\log \alpha_p = \frac{20475}{T} - 19.48$	$T_1 = \frac{10329T_2}{20475 - 7.77T_2}$

- € Each nonstoichiometric composition of a sample (x_2) is associated with strictly determined values T_2 and T_1 .
- € Under continuous change of T_2 or/and T_1 values, nonstoichiometric composition of a sample (x_2) varies continuously as well.

$$\frac{2\mu_{Ga}^{00}(T_2; x_2^0) - F^0(T_2)}{T_2} = \frac{1}{4} \left[\frac{2\mu_{Ga}^{00}(T_1; x_1^0) - F^0(T_1)}{T_1} \right] \quad \text{Eq 33}$$

- € Using large amount of the charge relative to the sample amount
- € Heterophase mixture made of two adjacent binary condensed phases (noteworthy, in a mixture of two coexisting phases, the chemical potential is "xed at a given temperature and does not depend on the overall composition of the mixture)

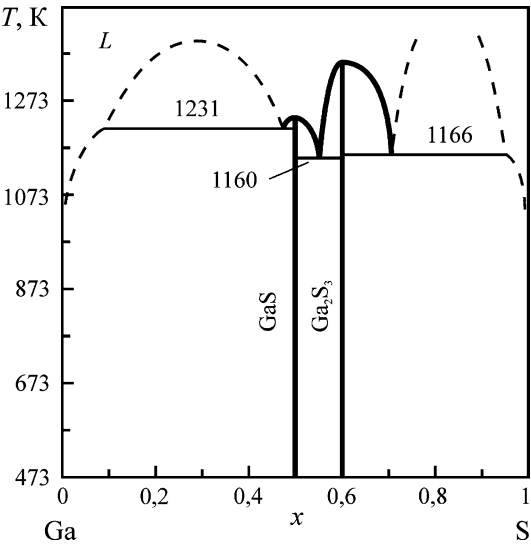


Fig. 2 T-x diagram of Ga-S system. Source Ref 17

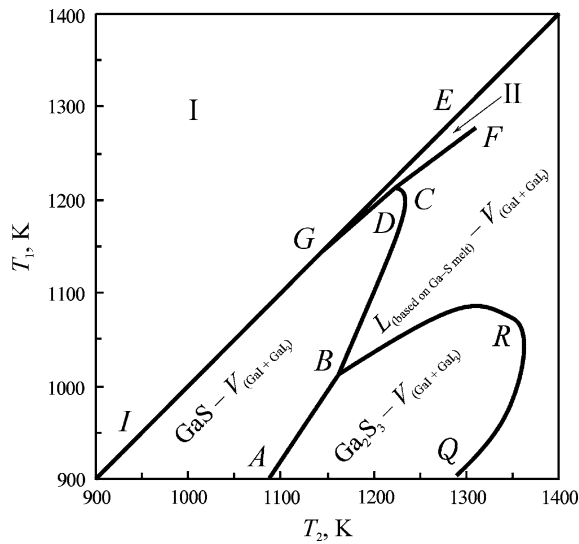


Fig. 3 Calculated boundary lines that limit areas of stability for phases in the Ga-S system. Lines of three-phase equilibria: AB-GaS-Ga₂S₃^s-V; BRQ-L-Ga₂S₃^{sol}-V; BCD-L-GaS^{sol}-V. Positions of the following lines are given tentatively: IE-Ga; DF-L-Ga^{liq}-V; GD-Ga^{liq}-GaS^{sol}-V, where L is melt of variable composition Ga_{1-x}S_x, Ga^{liq} is melt of practically pure gallium (see also Fig. 2), and V is vapor of Ga and Ga₂S₃. Field I - experimentally unattainable "field" where $T_1 > T_2$ (since T_2 should always be greater than T_1); Field II - area of co-existence of liquid (based on gallium) and vapor (Ga + Ga₂S₃) phases

4. Conclusions

€ Using the pure component (A in Eq 1) as a source/getter material

References

